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Development of operational strategies to remove carbon dioxide in photobioreactors

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ABSTRACT

The objective of this work was to evaluate different operational strategies for photobioreactors to remove carbon dioxide using the cyanobacteria, *Aphanothece microscopica Nägeli*. Two types of reactor configuration, bubble column and airlift were evaluated under three different operational conditions to treat air containing 15% carbon dioxide: simple operation, air recirculation and two sequential reactors. The results obtained showed that the reactor configuration and the operational mode were both determinant criteria for the performance of photobioreactors in the biological conversion of carbon dioxide. Operations with air recirculation showed possibilities for use in small-scale operations, but two-stage sequential photobioreactors (elimination capacity and removal efficiency of 12,217 $g_{carbon}/m^3_{reactor}$ day and 52.5%, respectively) were shown to be the operational mode with greatest potential for application on an industrial scale by the increased removal efficiency.

1. Introduction

Global atmospheric concentration of carbon dioxide increased markedly as a result of human activities [1]. Carbon dioxide is the most important anthropogenic greenhouse gas (GHG) and its concentration has increased from a pre-industrial value of about 280–379 ppm in 2005 [2]. The first regulations aimed at controlling atmospheric pollutants have already been implanted; the signing of the Kyoto Protocol in December 1997 is an historic step in reversing the increase in these emissions. The primary achievement of the Protocol is the commitment of countries referred in the Annex I to reduce their emission some 5% below their country specific 1990 level, in the period 2008–2012 with penalization clauses in case of non-compliance [3].

Biological carbon sequestration using technologies such as controlled photosynthetic reactions may help to alleviate GHG problems, by carrying out reactions in which the CO_2 is transferred to the aqueous phase of the system where microbial conversion occurs, resulting in the production of oxygen, biomass, soluble biopolymers, carbonate and bicarbonate and volatile organic compounds [4–6].

At this moment, the economic return for the operation of these systems may become feasible through the carbon credits [7] and by using the photobioreactor technology to produce biomass. The biochemical composition of the microalgal cells may be of commercial interest, possessing significant proportions of proteins, lipids, carbohydrates, pigments and nucleic acids, and could therefore be used as ingredients in foods destined for human consumption, animal feeds, extraction of biomolecules and in the production of biofuels [8–10].

In previous studies [11], we demonstrated that CO_2 removal by the cyanobacteria *Aphanothece microscopica Nägeli* in a bubble column photobioreactor was described by a first order kinetic model. In this study was determined that a 15% (v/v) content of CO_2 in the air inlet optimized CO_2 uptake performance. Furthermore, Jacob-Lopes et al. [12] showed that this inlet CO_2 concentration favoured the cyanobacterial growth when compared to a wide range of concentrations (3, 15, 25, 50 and 62%). In both studies, inlet airstreams with 15% CO_2 (v/v) were considered the best conditions for biomass growth and carbon dioxide removal, however, this condition leads to substantial losses of underutilized CO_2. So, operational strategies should be developed for improve the performance of the CO_2 utilization in photobioreactors.

Design and scale-up methodologies for photobioreactors have not been extensively described. Irrespective of the specific reactor configuration and operational mode employed, several essential issues need addressing: (i) effective and efficient provision of light;

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Nomenclature

EC	elimination capacity (g/m^3 min)
RE	removal efficiency (%)
C_i	inlet CO_2 concentration (g/m^3)
C_o	outlet CO_2 concentration (g/m^3)
C_R	CO_2 concentration in the reactor (g/m^3)
Q	gas flow (m^3/min)
V_R	volume of the reactor (m^3)
V_T	sum of the volumes of the balance tank and the reactor (m^3)
r	CO_2 consumption rate (g/m^3 min)
$d(CO_2)/dt$	CO_2 consumption rate in the balance tank (g/m^3 min)
HRT	hydraulic retention time = V_R/Q (h)

(ii) supply of CO_2 while minimizing desorption; (iii) selection of strains with high growth rate, tolerance to CO_2 and temperature; (iv) analysis and definition of operational conditions and (v) scalable photobioreactor technology [13–15].

Thus the objective of the present study was to evaluate the capacity of the cyanobacteria, *Aphanothece microscopica Nägeli* to treat air containing 15% carbon dioxide in two types of photobioreactors, bubble column and airlift, under three different operational conditions: simple operation, air recirculation and two sequential reactors.

2. Material and methods

2.1. Microorganism and culture medium

Axenic cultures of *Aphanothece microscopica Nägeli* (RSMan92) were originally isolated from the Patos Lagoon estuary, Rio Grande do Sul State, Brazil (32°01′S–52°05′W). Stock cultures were propagated and maintained on synthetic BGN medium [16]. The incubation conditions used were 25 °C, photon flux density of 15 μmol m^{-2} s^{-1} and a photoperiod of 12 h.

2.2. Photobioreactors

The diagram of the experimental apparatus used is shown in Fig. 1. The photobioreactors were constructed in 4 mm thick glass with similar geometry, dimensions and working-volume (WV). The systems had an internal diameter of 7 cm, height of 70 cm and nominal volume of 2.4 L. In the bubble column reactors (BCR) air was supplied through a 7 cm diameter sinterized glass plate. For the airlift reactors (ALR), the dispersion system consisted of a 1 cm diameter air diffuser located in the centre of the column. In these reactors, a concentric tube with an internal diameter of 3 cm and height of 50 cm was also used, located axially in the centre of the column and fixed at a distance of 5 cm from the diffuser.

In the systems with air recirculation, the BCR and ALR were connected through a pump to a 13.25 L balance tank. The balance tank was used to increase the initial CO_2 mass and was maintained in the dark, to avoid photosynthetic reactions. The flow leaving the tank was directed back to the reactors, resulting in a closed circuit. In the sequential reactors the gases exiting from the first column were fed to the second reactor.

2.3. Kinetic data

For each reactor, the experiments were carried out under three operational conditions: (i) simple operation, (ii) operation with air recirculation and (iii) operation with two sequential reactors. The tests were carried out using the bioreactors operating in an intermittent regime, fed with 2.4 L synthetic BGN medium. The experimental conditions were: initial cell concentration of 100 mg L^{-1}, isothermal reactor operating at 35 °C, photon flux density of 150 μmol m^{-2} s^{-1} and continuous aeration at 1 VVM (volume of air per volume of culture per minute) with air containing 15% CO_2. The kinetic data were monitored with respect to cell concentration, pH and CO_2 concentration every 12 h of cultivation during the growth phases of the microorganism. The tests were carried out in duplicate and the kinetic data referred to the mean of four repetitions.

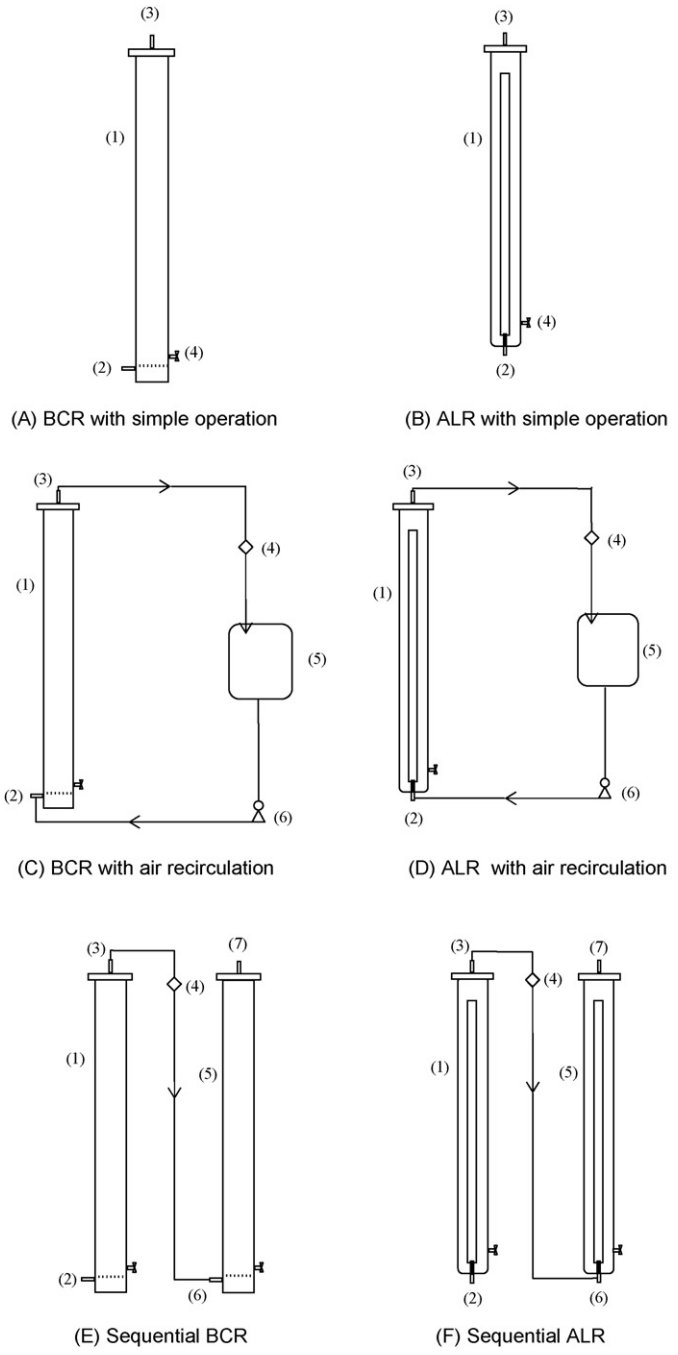

Fig. 1. Experimental apparatus. (A and B): (1) reactor; (2) gas entrance sampler; (3) gas exit sampler; (4) liquid sampler. (C and D) (1) reactor; (2) gas entrance sampler; (3) gas exit sampler; (4) air dehumidifier; (5) balance tank; (6) pump. (E and F): (1) reactor 1; (2) gas entrance sampler; (3) gas exit sampler; (4) air dehumidifier, (5) reactor 2; (6) gas entrance sampler; (7) gas exit sampler.

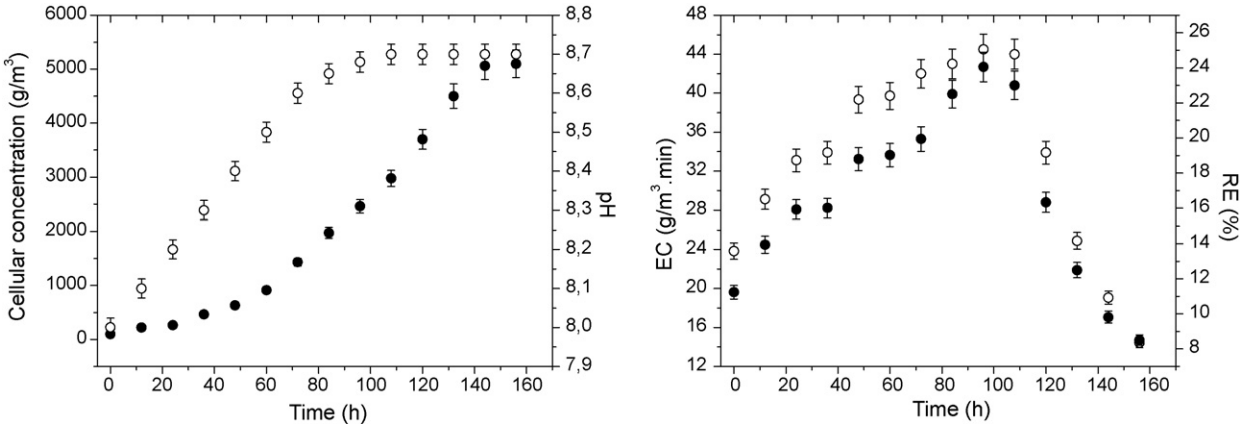

Fig. 2. Kinetic data for the BCR with simple operation (closed circle, cellular concentration and RE; open circle, pH and EC). Data points represent means ($n = 4$). Error bars indicate standard error from the mean.

2.4. Kinetic modelling

Elimination capacity and removal efficiency were used to describe the performance of a photobioreactors (simple operation and two-stage sequential reactors). Elimination capacity (EC) (Eq. (1)) is the mass of CO_2 removed per unit volume of reactor per unit time. Removal efficiency (RE) (Eq. (2)) is the fraction of the CO_2 removed by the photobioreactor, expressed as a percentage [17]. The numerical integration of EC with residence time using Simpson's 1/3 rule [18] was used to represent the total CO_2 removal.

$$EC = \frac{(C_i - C_o)Q}{V_R} \quad (1)$$

$$RE = \frac{C_i - C_o}{C_i} \times 100 \quad (2)$$

The kinetic modelling of the recirculation batch systems [19] consisted of establishing the mass balance for the whole system. It was considered that the volumes in the connecting lines and pump were negligible, that the reaction only occurred in the reactor, that the changes in CO_2 concentration at the entrance and exit to the reactor were small ($C_i - C_o$) and the system was well mixed. Thus Eq. (3) expresses the kinetic model for the reaction rate in a batch reactor with recirculation.

$$r = \left(\frac{V_R + V_T}{V_R}\right) \frac{d(CO_2)}{dt} \quad (3)$$

The validity of the proposed model was based on the differential operation criteria. In this sense, considering a constant feed rate (Q) and a CO_2 concentration in the reactor effluent of C_o, the concentration in the reactor would vary from C_i to C_o, and consequently $C_R - C_i$ when $(C_i - C_o) \rightarrow 0$. Accepting these suppositions, Eq. (3) is valid and the desired criterion in terms of the operational conditions and the removal rate is given by Eq. (4).

$$C_i - C_o = \frac{-V_R}{Q} \left(\frac{V_T}{V_R + V_T}\right) \times r \quad (4)$$

2.5. Analytical methods

The cell concentration was evaluated gravimetrically by filtering a known volume of culture medium through a 0.45 μm filter and drying at 60 °C for 24 h (accuracy of ±10%). Gas chromatography (GC) was used to determine CO_2 concentrations in airstreams. The equipment used was an Agilent Technologies chromatograph (series 6890) equipped with a column Porapack Q80/100, 6″ × 1/8″ S.S and a thermal conductivity detector (accuracy of ±1%). The operational conditions were as follows: injector and detector temperatures of 110 °C and column temperature of 65 °C. The carrier gas was helium with a flow rate of 25 mL/min. The sample volume injected was 100 μL. The CO_2 removed was determined from samples taken from the inlet and outlet gaseous phase of the system. The areas obtained using the integrator was compared with reference curves to determine the CO_2 concentrations. The photon flux density was determined using a digital photometer (Spectronics, model XRP3000, accuracy of ±5%), measuring the light incident on the external reactor surface. The flow rates of the CO_2, air and CO_2 enriched air were determined with rotameters (AFSG 100 Key Instruments, accuracy of ±5%).

3. Results and discussion

3.1. Batch reactors with simple operation

Photobioreactors are multi-phase physical–chemical–biological systems with numerous interactions between the process variables and the dynamic alterations between the gas–liquid–solid parts of the system [13]. The use of this type of reactor to eliminate CO_2 is considered a promising alternative, since carbon can be fixed by different mechanisms [20]. The kinetic data for the BCR with simple operation are expressed in Fig. 2.

The kinetic data for CO_2 removal expressed in terms of the EC and RE showed a gradual increase in CO_2 removal from the system up to a certain point, where the inorganic carbon elimination capacity started to decrease by the combined effect of nutrient depletion and reduced light availability due to absorption by the increasing cell population. The reduction in performance is further complicated by the formation of cell agglomerates in the later stages of the process associated to the exhaustion of the nutrients [21]. Cell agglomeration reduces CO_2 and nutrient availability and constitutes an additional resistance to mass transfer. When better mixing, it can be expected that less cell aggregation will occur and more uniform distribution of cells in the reactor will be achieved. Smaller cells diminish mass transfer resistance, leading to better cell nutrition [22]. Visual observations of the reactors during culture and after completion of the experiment showed cell deposition of in the walls of both BCR and the ALR, although it was more marked in BCR. These agglomerates yield lower CO_2 removal capacity by reducing light penetration, by increased mixing problems in the reactor and by their reduced area per unit of cell volume capable of receiving light energy for the subsequent carbon atom fixation reaction. Richardson and Jackson [23] reported that microalgal cells growing exponentially in agitated systems tended to form agglomerates during cell collisions. The rate of formation of these agglomerates depends primarily on the abundance and size of the cells. According to these authors, these characteristics determine the absorption

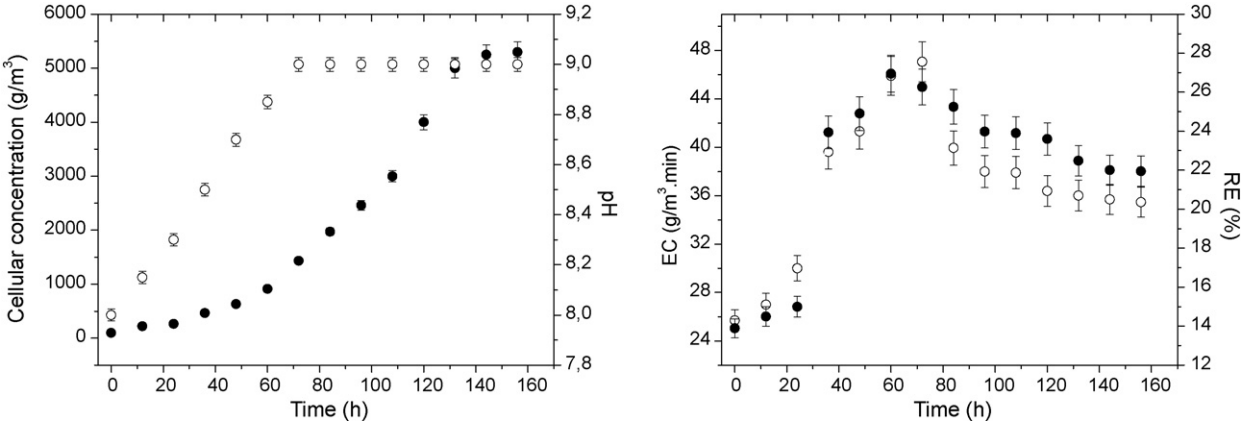

Fig. 3. Kinetic data for the ALR with simple operation (closed circle, cellular concentration and RE; open circle, pH and EC). Data points represent means ($n = 4$). Error bars indicate standard error from the mean.

and desorption flows of inorganic carbon in aqueous systems. Cultivations in steady-state conditions can be used for reduce these effects by maintaining of the cellular concentration and available nutrients.

In the simple operation mode maximum values of 44.5 g/m^3 min and 24.0% were obtained for the EC and RE, respectively, in 96 h of cell residence time. The maximum cell concentration and pH values obtained for the BCR were 5.1 g/L and 8.7, respectively. A gradual increase in pH associated with the cell mass is a characteristic of the cultivation of photosynthetic cells in photobioreactors. The pH variation in culture is mainly due to CO_2 uptake although variations due to consumption of other nutrients or degradation of the excreted metabolites may occur. Loss of dissolved CO_2 due to uptake into microalgal cells is partly compensated by regeneration from carbonates and bicarbonates. Consequently, CO_2 uptake is accompanied by changes in pH [24].

Similar behaviour was shown by the ALR using the simple operation (Fig. 3), in which the maximum values for EC and RE were about 46.4 g/m^3 min and 26.9%, respectively. These values were 4.1 and 10.7% higher than those obtained for the maximum elimination capacity and removal efficiency, respectively, using the BCR. These values differing significantly ($p < 0.05$) by Tukey test. In addition, throughout the period evaluated, the ALR was shown to be more efficient, indicating overall elimination capacities and removal efficiencies superior to those of the BCR. The maximum cell concentration and pH values obtained were about 5.3 g/L and 9.0, respectively. The better performance by the ALR can be related to the better fluidization, less growth on the reactor wall and less cell aggregation.

Among the many decisions involved in a CO_2 elimination system project, those concerning the configuration and operational mode of the reactor are fundamental to obtain elevated performance. Vertical column reactors are compact, low cost and easy to operate aseptically [15]. In addition, bubble and airlift systems are considered viable options for the biological CO_2 sequestration [25]. According to Jin and Lant [26] the basic difference between these two configurations is based on the air bubble distribution, with random bubble rising in the BCR, whereas in the ALR, the hydrostatic pressure difference between the riser and downcomer induces an ordered rise and fall of the air bubbles, and consequently of the cells. This type of movement produces more effective mixing and mass transfer in the liquid phase in the ALR as compared to the BCR. These considerations justify the better performance of the ALR as compared to the BCR, not only obtaining higher values for the elimination capacity and removal efficiency, but also showing better performance during critical process periods, where mixing became more difficult due to the formation of cell agglomerates.

In addition, simple CO_2 bubbling in the liquid phase does not lead to a total dissolution since a fraction of the injected CO_2 is lost in the gas outlet. CO_2 absorption is mainly a function of the volumetric mass transfer coefficient, the mass transfer driving force and the gas retention time [27]. According to Merchuk et al. [22] the amount of gas supplied to the reactor is the most important variable in pneumatic reactor operation. This parameter strongly influences the mixing of the liquid medium, the distribution of cells in the reactor, nutrient availability to cells and CO_2 absorption. While increased gas flow rates improve mixing and therefore mass transfer, it usually leads to a drop in the efficiency of CO_2 utilization

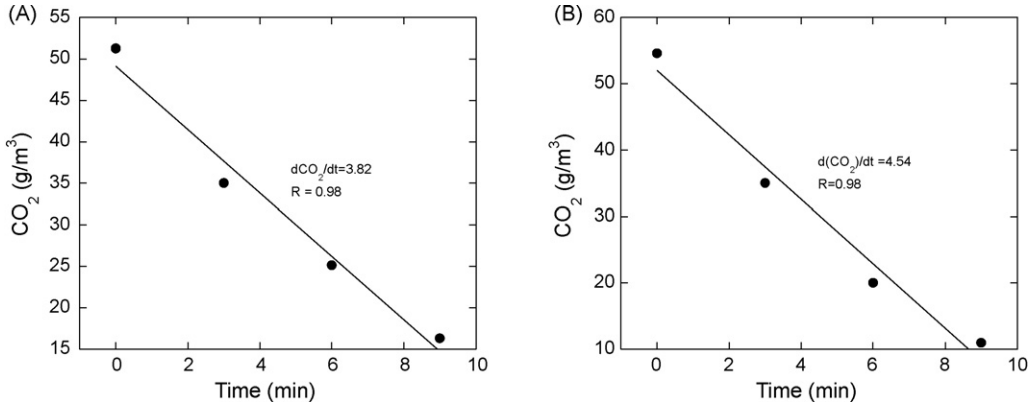

Fig. 4. Representative kinetics data for the BCR (A) and ALR (B) with air recirculation. BCR: HRT = 96 h, ALR: HRT = 72 h. Data points represent means ($n = 4$).

Table 1
Carbon dioxide removal kinetics in the BCR and ALR with recirculation.

HRT (h)	$-d(CO_2)/dt$ (g/m^3 min)	R	r (g/m^3 min)	$C_i - C_o$ (g/m^3)
Bubble column				
24	0.84	0.97	5.48	5.56
48	2.50	0.99	16.30	16.56
72	3.03	0.98	19.75	20.06
96	3.82	0.98	24.91	25.30
120	2.83	0.96	18.45	18.74
144	1.38	0.99	9.01	9.14
156	0.94	0.96	6.13	6.22
Airlift				
24	1.68	0.97	10.95	11.12
48	3.82	0.95	24.90	25.29
72	4.54	0.98	29.47	29.94
96	3.68	0.95	24.01	24.38
120	3.34	0.97	21.78	28.22
144	3.61	0.99	23.54	23.91
156	3.13	0.99	21.58	21.92

in bioreactors. The gas liquid transfer is obviously important, since it is responsible for the provision of CO_2 required as building blocks for the cells growth. This step however is relatively fast due to the high solubility of CO_2 in the liquid and the high concentration of CO_2 used. Within the liquid itself, far from the gas–liquid interface, two mechanisms of mass transfer can be distinguished. The first one is convective transfer that takes place throughout the reactor and is related to the total liquid circulation and mixing. This is a function of reactor design, physical properties of the medium and gas flow rate. The second one is the transfer from the bulk of the liquid toward the suspended cells. Shear phenomena and diffusion at the boundary between the cell and the medium basically limit this transfer.

Thus, for the efficient CO_2 sequestration and biomass production from photosynthetic cells, the design of a culture system with reduced carbon losses is needed. Most of the closed photobioreactors for the phototrophic production of microalgae attain CO_2 removal efficiencies under 30% and therefore, the injected CO_2 is mainly lost through the exhaust gas from the reactor [28]. In this sense, only by recycling the exhausting gas into the reactor or by sequential reactors these losses can be reduced.

3.2. Recirculating batch systems

Recirculating batch systems can present advantages in small-scale processes, the pollutants being recirculated in a closed circuit until the desired CO_2 uptake has been reached. According to Berenguel et al. [29], current CO_2 transfers technology in microalgal culture systems suffers the shortcomings of loss of valuable CO_2 in the exhaust air. In this sense, the recirculation of air is an important strategy for reuse of exhaust gas and for improvement of the efficiency of the systems, although lower mass transfer rates may be expected with the decreasing CO_2 concentrations found in the successive cycles. Table 1 shows the kinetic characterization for a batch BCR with air recirculation, as a function of the hydraulic retention time (HRT).

An analysis of the kinetic data showed a gradual increase in the removal rates of the recirculating CO_2 as a function of the HRT. For the BCR, the maximum consumption rates in the balance tank (3.8 g/m^3 min) were obtained after 96 h of cultivation. In parallel, considering the relationship between the volumes in the reactor and those in the balance tank, maximum CO_2 removal rates of 24.9 g/m^3 min were obtained, associated with a difference between the CO_2 concentration present in the tank and that at the exit to the reactor of 25.3 g/m^3 at the instant considered.

These data, when corroborated by those obtained in the BCR with simple operation, indicated that for these systems, the maximum CO_2 removal rates occurred after 96 h of culture. Lower removal rates were found in the system with recirculation, since the CO_2 removal rate is proportional to its concentration [11] which reduces with each passage through the recycling system. Adjustment of the proposed model was based on obtaining linear CO_2 concentration profiles in the balance tank as a function of time, in order to validate the considerations made. The high correlation coefficients obtained associated with Fig. 4A, supported these assumptions. Additionally, the differential operation criteria confirm the hypotheses raised.

Similar behaviour was shown by the ALR with recirculation (Table 1), the maximum CO_2 consumption rates obtained in the balance tank, removal rates from the system and difference in concentration ($C_i - C_o$) being 4.5 g/m^3 min, 29.5 g/m^3 min and 29.9 g/m^3, respectively. However in this system the maximum removal rates were obtained after 72 h of cell residence time, representing a 15% reduction in the time required to reach maximum removal rate, as compared to the BCR. In addition, the maximum removal rates achieved by the ALR were 15.5% higher than those achieved by the BCR, proof of the superior performance of the ALR. Fig. 4B shows the fit of the experimental data for the ALR, which, together with the correlation coefficients obtained and differential operation criteria demonstrated the validity of the model used.

In addition, it should be considered that the air recirculation causes the accumulation of photosynthetically produced oxygen that may eventually damage growth, so a system to remove the excess of O_2 can be required. Absorption of the excess oxygen in sodium bisulphite solution was demonstrated to be useful for this purpose [30].

The principal advantage of this operational mode is related to the possibility of obtaining elevated values for removal efficiency, since the closed circuit allows for manipulation of the total removal rate. Industrially this type of operation is limited by the low pollutant elimination capacity. Thus for larger volumes, continuous systems with recirculation may be more appropriate [31].

3.3. Two-stage sequential photobioreactors

The efficiency of using the CO_2 transferred to the liquid phase of photobioreactors is an important parameter in the performance of these processes. This factor depends both on the metabolic capacity of the cells and on the environmental conditions (pH, temperature, nutrients, light availability, presence of inhibitors, etc.) To foster more efficient CO_2 utilization, longer residence time can be used with sequential reactors. This alternative shows some advantages over the selection of a longer reactor both by kinetic [32] and design considerations [29].

The kinetic parameters for cell growth (data not show for brevity) and CO_2 removal (Fig. 5) in two sequential BCR indicate that the first reactor has significant higher biological activity when compared to the second reactor which is in contact with lower CO_2 concentrations due to the uptake of in the first reactor. Longer retention time allowed attaining around 45% CO_2 removal efficiency. A similar trend was found for the sequential ALR (Fig. 6) but with slightly better performance. In this case, the maximum value for removal efficiency was close to 52.5%. These results suggested that under the conditions studied, gas–liquid mass transfer limitations were not very relevant and that working in series results in minimizing CO_2 losses and improving the removal efficiency. Similar results were observed by Rubio et al. [33], in which the losses of CO_2 declined with increasing length of the tube. Whereas up to 30% of the injected CO_2 would be lost in a system with a 50 m long, the losses could be reduced to about 5% if the length were increased to 150 m. This is simply because a longer tube allows more gas–liquid contact time for mass transfer and consumption. These

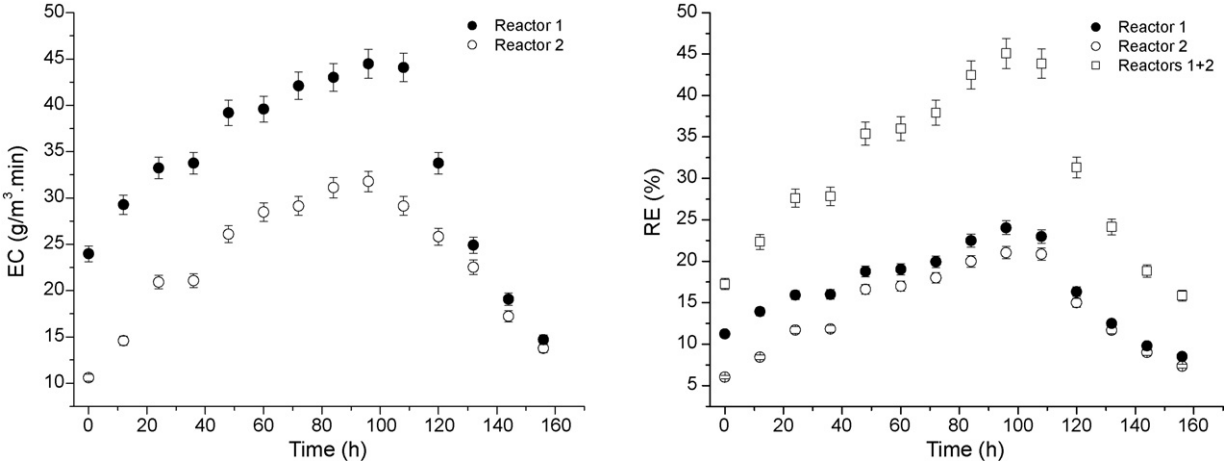

Fig. 5. Kinetic data for two sequential BCR. Data points represent means ($n = 4$). Error bars indicate standard error from the mean.

Table 2
Daily carbon sequestering capacity of the reactors.

System	Carbon sequestered ($g_{carbon}/m^3_{reactor}$ day)
BCR (simple operation)	13,046 ± 150
BCR (with air recirculation)	5,612 ± 160
BCR (sequential)	10,929 ± 180
ALR (simple operation)	14,495 ± 120
ALR (with air recirculation)	8,765 ± 100
ALR (sequential)	12,217 ± 90

lower carbon losses imply that the culture would be approaching carbon limitation.

3.4. Overall carbon sequestration capacity

Total carbon sequestration capacity by the systems was obtained by integrating the respective EC and is represented in Table 2 considering reactor working-volumes of 1.0 m^3. An analysis of the results obtained showed the superior performance of the ALR in all the operational modes used, when compared to the bubble column reactors.

The performance of the photobioreactors in CO_2 sequestration is dependent mainly of the microalgal species, CO_2 concentration in the inlet air stream, photobioreactor configuration, and operational mode [34,35]. Cheng et al. [36] have demonstrated maximum elimination capacity of 6.24 g_{carbon}/m^3 day at 1% CO_2 in a membrane photobioreactor with *Chlorella vulgaris*. These same authors reported a removal efficiency peak of 55.3% at 0.15% CO_2. Chiu et al. [37] obtained a maximum elimination capacity of 4.8 g_{carbon}/m^3 day at 15% CO_2 using a bubble column photobioreactor with *Chlorella* sp. The same study also reports removal efficiencies of 58% with 2% inlet CO_2. Fan et al. [38] obtained maximum elimination capacity of 1.68, 0.96, 0.72 and 0.24 g_{carbon}/m^3 day at 1% CO_2, in a membrane, airlift, bubble column and membrane contactor photobioreactors, respectively, using a culture of *Chlorella vulgaris*. Keffer and Kleinheinz [39] reported overall average elimination capacity of 1534.0 g_{carbon}/m^3 day using *Chlorella vulgaris*, when exposed to an air stream with over 1850 ppm CO_2 (removal efficiencies of 74%).

The results in the present study with *Aphanothece microscopica Nägeli*, show in general higher elimination capacities than those reported elsewhere at high CO_2 concentrations in the feed gas. Preliminary studies have demonstrated that besides biomass formation, precipitation of bicarbonates and secretion of biopolymers into the culture media, the cyanobacteria can partially convert carbon dioxide into volatile organic compounds (data not shown).

Finally, to assess process performance both removal efficiency and elimination capacity should be considered and a trade-off, generally determined by economic considerations, must be established between both parameters in the selection of particular configurations [16,40].

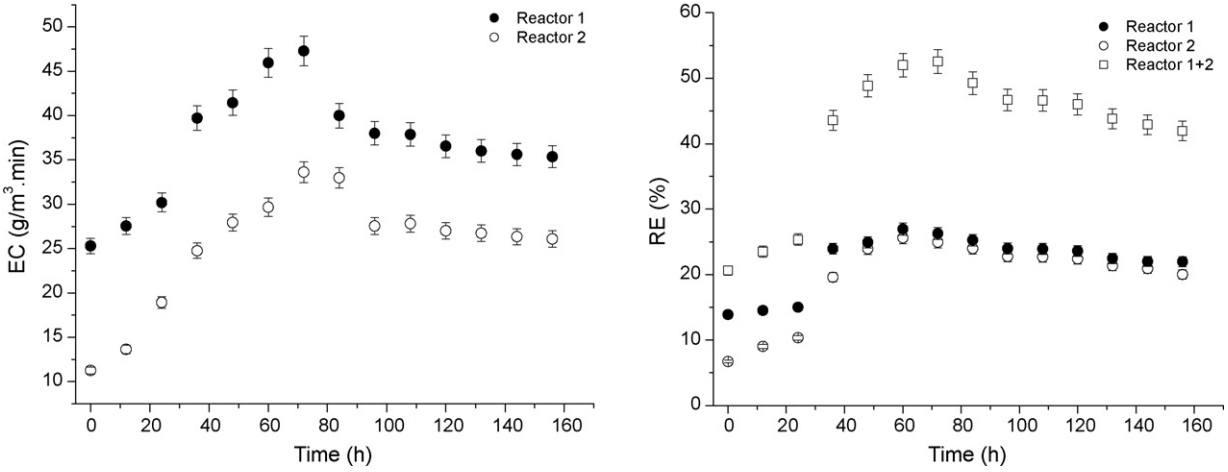

Fig. 6. Kinetic data for two sequential ALR. Data points represent means ($n = 4$). Error bars indicate standard error from the mean.

4. Conclusions

The mitigation of greenhouse gas emissions, especially CO_2, represents an important aspect in the sustainable development of industrial activities. CO_2 sequestration by photosynthetic reactions may be an adequate strategy from this point of view, since it can be transformed into various products which can be reused in different ways. In the present study, the development of operational strategies and the project of reactors for use in the biological conversion of CO_2 by the cyanobacteria *Aphanothece microscopica Nägeli* were considered. The mixing conditions in ALR favoured greater CO_2 removal by limiting growth on the reactor walls and cell agglomeration. Improved removal was shown to be feasible with both sequential reactors or CO_2 recycling, but imply reduced volumetric rates as the liquid concentrations diminish.

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